POLYMER BRUSHES: FABRICATION, NANOPATTERNING, ACTUATION AND SENSING

Marian Kaholek, Nehal Abu-Lail, Woo-Kyung Lee, Robert L. Clark, and Stefan Zauscher[*]
Dept. of Mechanical Engineering and Materials Science, Duke University, Durham, NC 27708

Sang-Jung Ahn
Dept. of Computer Science, Duke University, Durham, NC 27708

Kalle Levon
Polymer Research Institute, Polytechnic University, Brooklyn, NY 11201

Bruce LaMattina[*]
Army Research Office, Research Triangle Park, NC 27709

1. INTRODUCTION

We present new strategies to fabricate patterned polymer brush arrays on the micrometer and nanometer length scale by combining common lithography methods, such as scanning probe lithography (SPL) and electron beam lithography (EBL), with surface-initiated polymerization. We studied the mechanics of microcantilevers decorated with stimulus-responsive polymers (SRP) and demonstrated their possible use as sensors, amplifiers, and actuators. The use of SRP brush arrays and coated micro-cantilevers promises great potential for sensing and actuation applications in micro-fluidic and Bio-MEMS devices because of the unique way by which SRPs amplify molecular binding events and changes in the solvent environment. This is significant for the Army, where fast and simple detection of biological agents is critical for soldiers in the field. To date, little research has been done on using the conformational change of polymer thin films to amplify and transduce biological binding events. All of these concepts could be incorporated with "smart", self-sensing, piezoelectric cantilevers. Ultimately, this can lead to field-deployable, reliable, cost-effective, nanobiosensors for the detection of, for example, protein-ligand interactions.

Patterned polymeric and biomolecular nanostructures on surfaces have attracted significant research interest due to their potential uses in a wide range of applications, including biosensors and biomimetic materials. Several studies explored micro- and nanofabrication of polymeric structures in a "grafting from" approach using microcontact printing, photolithography, chemical lithography, contact molding, scanning probe lithography (SPL), and electron-beam lithography (EBL). Although significant progress has been made in the templated fabrication of polymer brushes, preparation of precisely patterned, surface attached polymeric micro- and nanostructures with controlled chain length, chemical functionality, shape, feature dimension, and inter-feature spacing is still in the developmental stage.
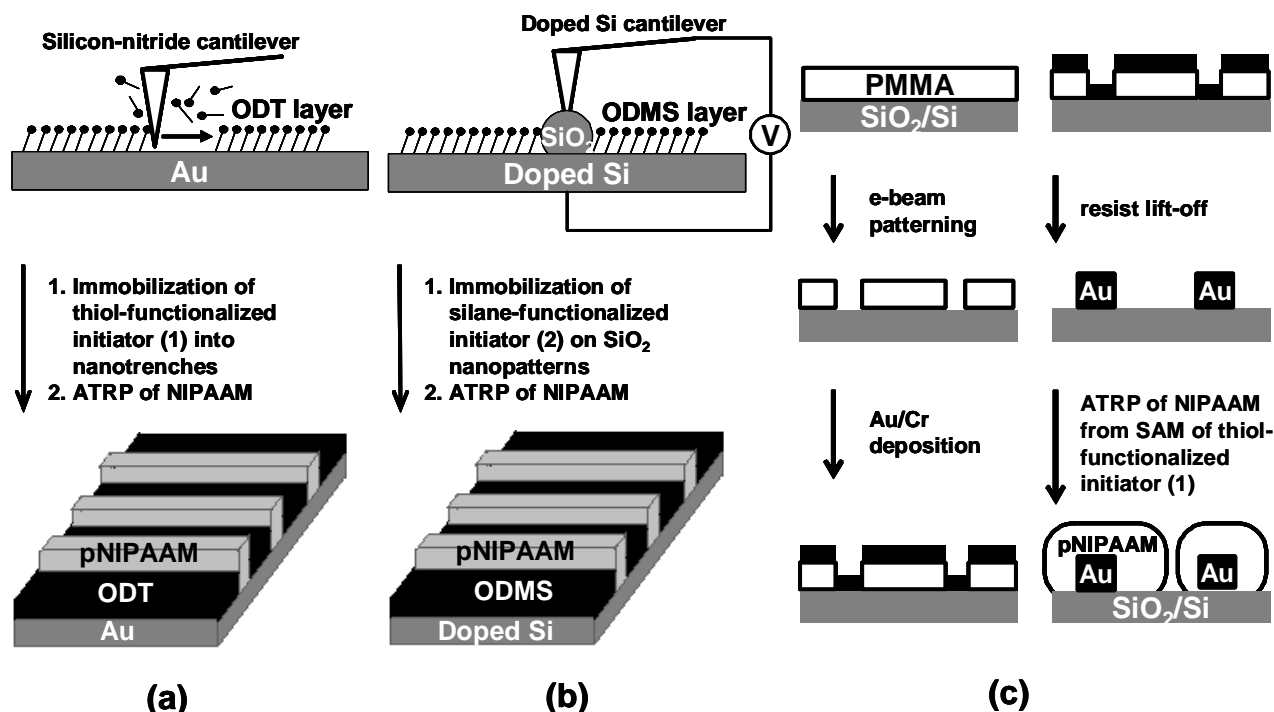
In recent years there has been a proliferation of micro-cantilever based sensors because of their simplicity, and ability to function in small sample volumes. We show that micro-cantilevers, decorated on one side with poly(N-isopropylacrylamide) (pNIPAAM) brushes responded to changes in solvent type, whereas cantilevers decorated with a copolymer composed of 70% NIPAAM and 30% vinylimidazole (VI) respond sensitively to changes in solution pH. The stimuli-responsive polymer (SRP) brush acts as a transducer with a significant potential of "amplification". We believe that decoration of the polymer brush structure with a particular peptide sequence may enable the fabrication of sensitive biosensors for the detection of spores or viruses.

2. METHODS

1. Nanopatterning of Thiol Initiator by Nanoshaving

A self-assembled monolayer (SAM) of octadecanethiol (ODT), forming a hydrophobic resist layer on gold coated silicon substrates, was prepared by immersion of substrates in a 1mM ethanolic solution of ODT for 48 h. The ODT SAM was patterned by "nanoshaving" (Liu et al., 2000); i.e, by directed mechanical ablation of the ODT resist using an AFM where a silicon-nitride (Si_3N_4) AFM cantilever was used in contact mode (Scheme 1a). We applied large normal forces and high scan speeds to remove the resist and create a pattern of straight "trenches" on the substrate surface. The extent of resist removal was controlled by varying the shaving time while maintaining a constant scan speed of 20 µm/s. Subsequently, the freshly exposed gold surface in these trenches were backfilled by immersing the substrate for short time period in a 1mM ethanolic solution of the thiol initiator (1), ω-mercaptoundecyl bromoisobutyrate

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Scheme 1. Preparation of surface-confined pNIPAAM polymer brush nanopatterns by combining (a) AFM nanoshaving, (b) AFM anodization lithography, and (c) lift-off electron beam lithography with surface-initiated polymerization using a surface-tethered initiator.

$(BrC(CH_3)_2COO(CH_2)_{11}SH)$, to form an initiator pattern of parallel lines. The substrate was then sonicated in ethanol and finally dried in a stream of nitrogen.

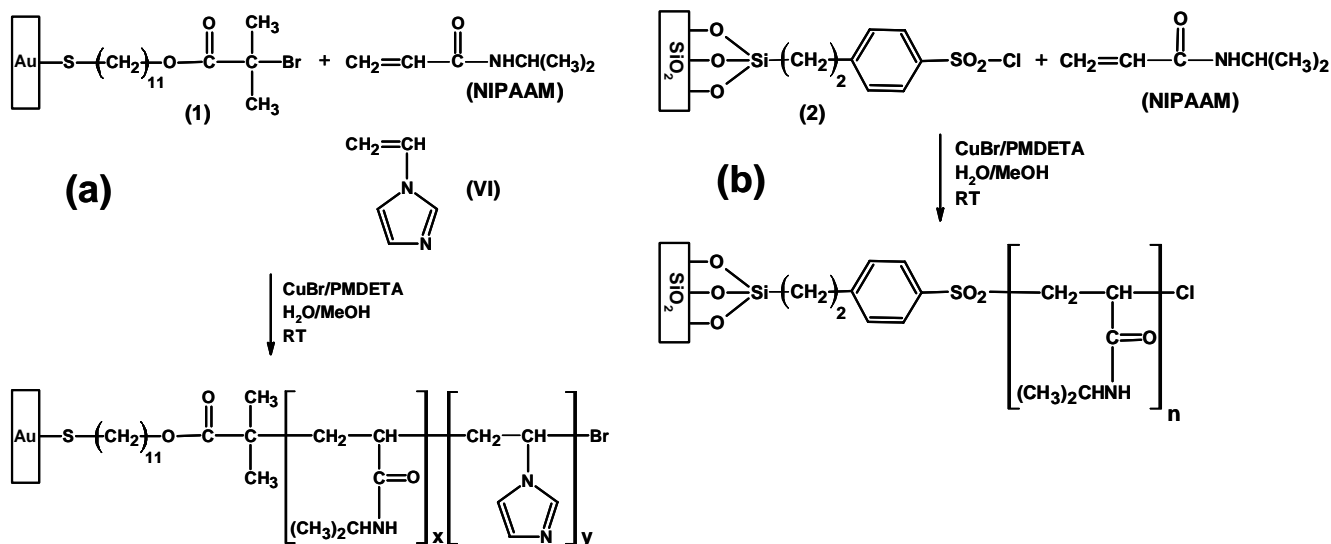## 2. Nanopatterning of Silane Initiator by Anodization Lithography

The silicon substrates were cleaned with piranha solution $(H_2O_2:H_2SO_4, 1:3)$ at 80°C, and then washed thoroughly with water and ethanol. The cleaned silicon surface was immersed in an aqueous solution of NaOH (0.1 M) and subsequently in an aqueous solution of HNO_3 (0.1 M) to generate hydroxyl groups. The surface was then incubated with octadecylmethyldiethoxysilane (ODMS) in hexane (0.1 M) for 12 h at 65°C. After incubation, the surface was sonicated in ethanol and dried in a stream of nitrogen. The silicon oxide nanopatterns were generated by anodization lithography (Snow et al., 1995), applying a bias voltage to the silicon substrate (Scheme 1b). Line patterns were generated under a bias voltage of 10 V with 4 sec writing time. The lithographic conditions were fixed to generate consistent volume expansion of silicon oxide patterns to an average height of 1 nm. The relative humidity during lithography was ranged between 35 and 55%. To attach silane-initiator on patterned area, the samples were incubated in a 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CTS) initiator (2) in an anhydrous dichloromethane (0.1 M) at room temperature for overnight, sonicated in dichloromethane and finally dried in a stream of nitrogen.

3. Nanopatterning of Thiol Initiator by Lift-Off Electron Beam Lithography

The electron-sensitive resist film of poly(methyl methacrylate) was spin-coated onto cleaned Si substrate and annealed at 160 °C on a hot plate for 20 min. The resist layer was then patterned by exposure to an electron beam, using a Philips FEI XL30 Thermal Field Emitter SEM controlled by Nano Pattern Generator System (NPGS) software. The exposed PMMA layer was developed in a solution of methyl isobutyl ketone and isopropyl alcohol (1:3, v:v) A layer of chromium and a layer of gold were thermally evaporated onto the patterned PMMA/silicon substrate under a vacuum at room temperature to obtain geometrically well-defined gold features on the exposed SiO_2 surface. The Au-coated, developed resist was lifted-off (Howard et al., 1980) by immersing the substrate in boiling acetone leaving behind 40 nm thick Au patterns on the silicon substrate (Scheme 1c). The SAM of the thiol-initiator (1) on the gold patterns was obtained by immersing the substrate in a 1 mM ethanolic solution of the thiol initiator (1) for 48 hrs.

4. Cantilever Deflection Measurements
The deflection measurements were performed in the fluid cell of an atomic force microscope (MultiMode, Nanoscope III controller, Veeco). Commercially available "V"-shaped Si_3N_4 micro-cantilevers (196 µm long and 500 nm thick), gold coated on their backside, were used.

Scheme 2. Surface-initiated polymerization of (a) NIPAAM and NIPAAM-VI (7:3) on gold surfaces using surface-tethered thiol initiator (1), and (b) NIPAAM on silicon substrates using surface-tethered silane initiator (2).

The force constant of each cantilever was determined individually before an experiment from the power spectral density of the thermal noise fluctuations. Measured spring constant values varied between 60-78 pN/nm. To avoid tip-surface interactions, the cantilever was placed at least 100 microns above the surface. Cantilever deflection was measured by monitoring the position of the laser beam reflected from the free end of the cantilever onto a photosensitive detector. The initial position of the cantilever was set to read 0 V on the photodetector. Readings were taken approximately every 45 seconds until the deflection of the cantilever reached an equilibrium state. Cantilever deflection voltage was converted to true deflection values (in nm) by multiplying with the photodetector sensitivity, typically about 90 nm/V. Deflection measurements were performed on bare, gold coated silicon nitride cantilevers and on cantilevers decorated with stimulus responsive polymer brushes with different thickness at room temperature, such as temperature/solvent sensitive pNIPAAM and pH sensitive pNIPAAM-VI (7:3).

5. NIPAAM and NIPAAM-VI Polymerization

Poly(*N*-isopropylacrylamide) (pNIPAAM) nanopatterns on gold surfaces (Scheme 2a) and on silicon surfaces (Scheme 2b) and micro-cantilevers decorated on one side with pNIPAAM and poly(*N*-isopropylacrylamide-*co*-1-vinylimidazole) copolymer (PNIPAAM-VI) brushes (Scheme 2a) were prepared by surface-initiated atom transfer radical polymerization (ATRP) (Matyjaszewski et al., 2001). In this process, gold and silicon substrates decorated with patterns of thiol (1) and silane (2) initiator, respectively, and thiol initiator (1) modified cantilevers were immersed in the polymerization solution for a specified time period at room temperature under a nitrogen atmosphere. Prior to use, all solutions and flasks were thoroughly flushed with nitrogen to remove oxygen. The polymerization solution was prepared by adding a solution of monomer to an organometallic catalyst. The organometallic catalyst was formed in a nitrogen atmosphere by adding Cu(I)Br and PMDETA in a 1:5 molar ratio to methanol (MeOH) as solvent. For the preparation of a pNIPAAM brush, 18% (wt) aqueous solution of NIPAAM monomer was filtered into the catalyst-complex solution through a 0.45 µm Millipore Millex filter. For the preparation of a PNIPAAM-VI (7:1) brush, 14% (wt) NIPAAM monomer was filtered into the catalyst-complex solution and the polymerization solution was then transferred into flasks containing the micro-cantilevers to start polymerization. In a second step, VI monomer was injected into the same flask to give a concentration of 4.7% (wt). We used a PMDETA to CuBr molar ratio of 5:1 to suppress competitive coordination of pNIPAAM and pNIPAAM-VI to copper. The molar ratio of NIPAAM to Cu(I) was fixed at 4300:1. Nanopatterned pNIPAAM brushes and micro-cantilevers decorated with polymer brushes were prepared by polymerization for 60 to 90 minutes, and 10 to 30 min, respectively. The substrates were then removed from the polymerization solution and immediately rinsed with Milli-Q™ water to remove all traces of the polymerization solution, and subsequently dried under a flow of nitrogen.

3. RESULTS AND DISCUSION

1. Amplification of AFM Nanoshaving Pattern

Stimulus-responsive, surface confined pNIPAAM brush nanopatterns were prepared on gold-coated silicon
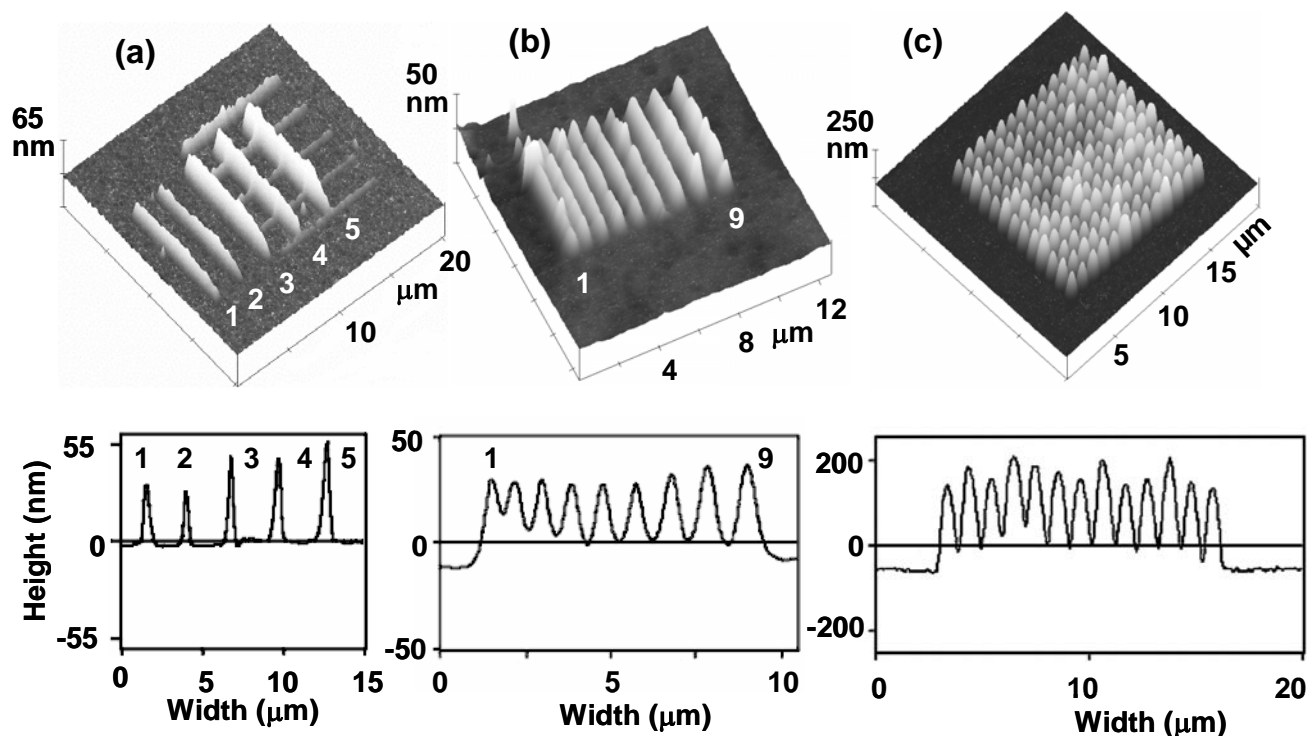
Figure 1. AFM height images of a pNIPAAM brush nanopatterns obtained at room temperature in water and corresponding average height profiles. The polymer brush patterns were fabricated by combining (a) AFM nanoshaving, (b) AFM anodization lithography, and (c) lift-off electron beam lithography with surface-initiated polymerization using a surface-tethered initiator.

substrates in a "grafting-from" approach (Kaholek et al., 2004) that combines "nanoshaving", a scanning probe lithography method, with surface initiated polymerization (Scheme 1a, Figure 1a). Figure 1a shows a typical pNIPAAM brush line-pattern imaged in water with line-widths of about 500 nm. The polymer brush heights obtained from averaged height profiles of lines 1 - 5 in Figure 1a, not only depend on the solvent (discussed below) but also on the nanoshaving conditions such as tip force and shaving time. Figure 1a shows that brush height increases with increasing shaving time (indicated in minutes directly by the line number) assuming that the shaving force has remained approximately constant. For example, the average heights of line 1 (1 min shaving) and line 5 (5 min shaving) in water, are 34 nm and 60 nm, respectively. This dependence of brush height on shaving time is likely associated with the degree of resist removal, where at short shaving times the number of residual thiol resist molecules is larger than that at long shaving times. The degree of resist removal will directly affect the initiator surface density that can be achieved by backfilling. Brush height is a function of initiator surface density, where low initiator densities lead to low brush heights. The conformation of nanopatterned pNIPAAM brushes is significantly affected by the solvent conditions. When exposed to water at room temperature, dry pNIPAAM brushes swell significantly and more than double their height. After addition of 50% (v) MeOH as a

cosolvent to pure water the average height decrease by 2 to 3 times. The averaged widths of the pNIPAAM line-patterns are affected only slightly by the solvent conditions. Our findings are thus consistent with the expected behavior of laterally confined and covalently attached stimulus-responsive polymer chains, where chain mobility is largely restricted to the out-of-plane direction.

2. Amplification of AFM Anodization Pattern

In a complementary approach pNIPAAM brush nanopatterns were prepared on silicon substrates in a "grafting-from" approach that combines AFM anodization, a scanning probe lithography method, with surface initiated polymerization (Scheme 1b, Figure 1b). AFM anodization lithography has been used to generate silicon oxide nanopatterns on silicon substrates by electrochemical anodic oxidation, in which an electric potential is applied between the conductive AFM cantilever and the resist ODMS layer in order to degrade a resist SAM. These lead to nano-oxidation on tip-contacted area for subsequent silane modification. This technique is particularly interesting because technologically important substrates, such as silicon, can be used. An important factor of a resist SAM is its ability to transfer electrons from the tip to the substrate. The organosilane based resist SAM used here is known to provide not only thin and uniform monolayers but also high spatial resolution during anodization lithography. The ODMS resist was
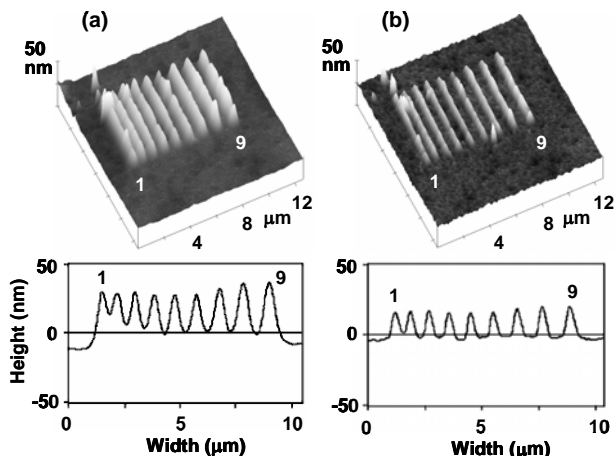
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Figure 2. AFM height images and corresponding average height profiles of a pNIPAAM brush line nanopattern imaged at room temperature in (a) water, and (b) a mixture of methanol/water (1:1, v:v). The pNIPAAM line pattern was fabricated by combining AFM anodization lithography with surface-initiated polymerization.

chosen because it forms a stable monolayer where methyl-terminated SAMs tend to be less reactive and render the surface hydrophobic, impeding the formation of a water meniscus between the tip and the surface. We controlled the lithographic conditions to generate an anodic oxide nanopattern with a vertical expansion of 1 nm. The effect of solvent conditions on the conformation of patterned, stimulus-responsive pNIPAAM brushes is demonstrated in Figure 2. In pure water and at temperatures below the LCST, pNIPAAM brushes are in a good solvent and the brush adopts an extended conformation with height of about 40 nm. After exposure to a water-MeOH (1:1, v:v) mixture (poor solvent), the brush adopts a hydrophobically collapsed conformation with height of about 20 nm. Figure 2 shows a typical pNIPAAM brush line-pattern with line-width of about 400 nm.

3. Amplification of EBL Pattern

Scheme 1c illustrates our "top-down/bottom-up" approach for fabricating patterned polymer brush arrays on the nanometer length scales (Ahn et al., 2004). In this approach, a silicon surface is patterned with gold (Au) using lift-off (dissolution) electron-beam lithography ("top-down") and the resulting pattern is then amplified by surface-initiated polymerization ("bottom-up") from immobilized thiol initiator (1) (Scheme 2a). Our approach has several advantages over existing polymer nanopatterning methods. First, patterns with well-defined feature dimension, shape, and inter-feature spacing can be created easily over large areas by lift-off EBL. Second, Au-patterned silicon substrates facilitate the fabrication of mixed polymer brushes with high lateral resolution by using silane- and thiol-containing initiators, immobilized

onto silicon and gold surfaces, respectively. Figure 1c shows a typical pNIPAAM brush dot-pattern with dot-width of about 550 nm imaged in water. The reversibility of the stimulus-responsive conformational change of nanopatterned brushes was observed by cyclic exposure to water, and water-methanol mixtures (1:1, v:v). In our patterning approach lateral brush growth on the sides of the 40 nm high gold templates needs to be considered. This can potentially compromise the lateral feature resolution of nanopatterned polymer brushes and can interfere with an adjacent features.

4. Solvent Sensitive PNIPAAM Modified Cantilever

The change in cantilever bending is a direct result of the change in the surface stress of the polymer brush layer. The surface stress in the polymer brush changes due to osmotic pressure and conformational changes in the polymer brush associated with changes in the solvent conditions. The deflection of cantilevers decorated with pNIPAAM polymer brushes was measured in water and in a mixture of water-methanol (1:1, v:v). Figure 3a shows the time response of the deflection of a pNIPAAM polymer brush decorated cantilever as a function of solvent condition. The measured cantilever deflection was larger for the brush in an extended conformation when exposed to water at room temperature (good solvent) than for the brush in a hydrophobically collapsed conformation when exposed to water-MeOH (1:1, v:v) (poor solvent). On average, deflection values measured in good solvent were 60 % larger than deflection values measured in the poor solvent. Changes in cantilever deflection were reversible upon cycling of the solvent conditions. Figure 3b shows the cantilever bending response at steady state as a function of brush height and shows that a thick brush causes more deflection than a thin one. Repeated experiments with different cantilevers showed that the magnitudes of cantilever deflection at steady state (including the thermally induced deflection) are reproducible upon solvent cycling. The change in the integral stress that causes the deflection of the cantilever was evaluated using Equation 1 (Petersen et al., 1999)

$$\sigma = E_s t_s^3 \frac{d}{6t_f(t_s + t_f)L} \tag{1}$$

where σ is the integral surface stress in J/m^2, E_s is Young's modulus of the cantilever (180 Gpa), t_s is the cantilever thickness (500 nm), t_f is the polymer brush thickness in m, L is the cantilever length (196 µm), and d is the differential deflection (the deflection resulting from the polymer brush only) in nm. We calculated the change in the integral stress that causes cantilever bending to range from 25 to 70 J/m^2 for the pNIPAAM brush decorated cantilevers. These values are significantly larger than those reported (Fritz et al., 2000) for thin SAMs (0.032 J/m^2) suggesting that the SRP brush acts as
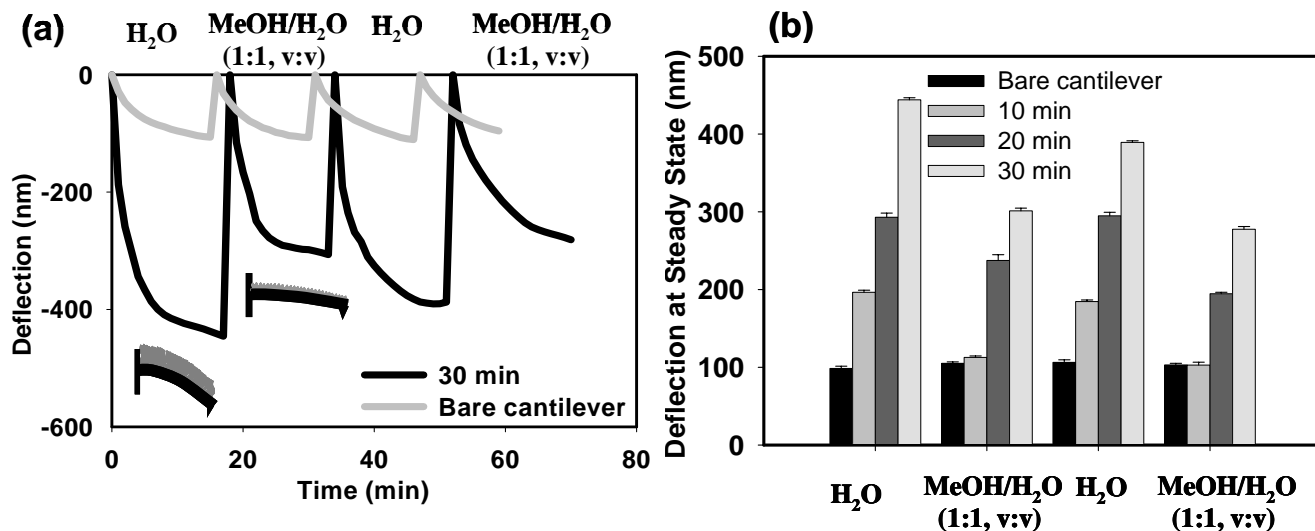
Figure 3. (a) An example on the output of deflection measurement performed on a micro-cantilever decorated with a pNIPAAM polymer brush (black line) grown for 30 minutes and a bare, gold coated silicon nitride cantilever as the control experiment (gray line) at room temperature in water and a mixture of methanol/water (1:1, v:v). (b) A histogram of the absolute steady state deflections of micro-cantilevers decorated with pNIPAAM polymer brushes of different heights by cyclic exposure (two cycles) to first water (brush swollen) and then to a 1:1 (v:v) methanol/water mixture (brush collapsed). The deflection values of a bare cantilever are shown also in different solvent for comparison purposes. The insets illustrate schematically the deflection of micro-cantilever decorated with pNIPAAM polymer brush upon changing of the solvent conditions.

a transducer with a significant potential of "amplification". Cantilever deflection at steady state stems from the osmotic pressure in the brush and is thought to be related to two factors, (1) polymer conformation and (2) polymer brush height (molecular weight). Based on the combination of these two factors one can construct a sensitivity criterion to design cantilever based sensors that employ SRP to sense changes in the solvent conditions. Interestingly, the relative change in cantilever deflection when cycled between good and poor solvent is approximately independent of brush height. This is a surprising result that suggests that already thin SRP brushes are sufficient to elicit a significant sensing response.

5. pH Sensitive PNIPAAM-VI Modified Cantilever

Similarly, deflection measurements were performed on bare, gold coated cantilevers and on cantilevers decorated with a pH sensitive polymer brush. The deflection of cantilevers decorated with pNIPAAM-VI (7:3) polymer brushes was measured at room temperature in solutions that ranged from pH 4.0 to 7.0. Figure 4a shows the time response of the deflection of pNIPAAM-VI brush decorated cantilever as a function of pH. Measured cantilever deflection was higher at lower pH values. This is expected since pNIPAAM-VI brush is known to change its conformation upon changing the pH of the solution. The brush extends with decreasing pH as a result of the conversion of the neutral imidazolyl groups into the protonated form. Therefore the swelling and

deflection is directly related to the ionic concentration in the brush as implied by the different pH. Figure 4b shows the cantilever bending response at steady state as a function of pH for the two different cantilevers. The cantilever bending response is approximately linearly dependent on brush height in the pH range of 4-6 with a large sensitivity (~ 121 nm/ pH unit) and remains unchanged in the pH range of 6-8. The change in the integral stress that causes cantilever bending ranged from 35 to 99 J/m^2 for the pNIPAAM-VI brush decorated cantilevers, also suggesting that the SRP brush acts as a transducer with a significant potential of "amplification".

4. CONCLUSIONS

In summary, we have demonstrated the prototypical fabrication of nanopatterned, surface-confined, stimulus-responsive polymer brushes on silicon and gold surfaces using a simple strategy that combines common lithography methods, such as scanning probe lithography (SPL) and electron beam lithography (EBL), with surface-initiated polymerization. Although the minimum attainable dimension of patterned features has not yet been explored, we expect that further improvements in the SPL and EBL process will result in considerably reduced feature dimensions. The advantages of lift-off EBL techniques are a precise control of pattern dimension, shape, and inter-feature spacing over large areas, and relatively fast lithographic speed. The advantages of SPL are that it allows patterning under ambient environmental
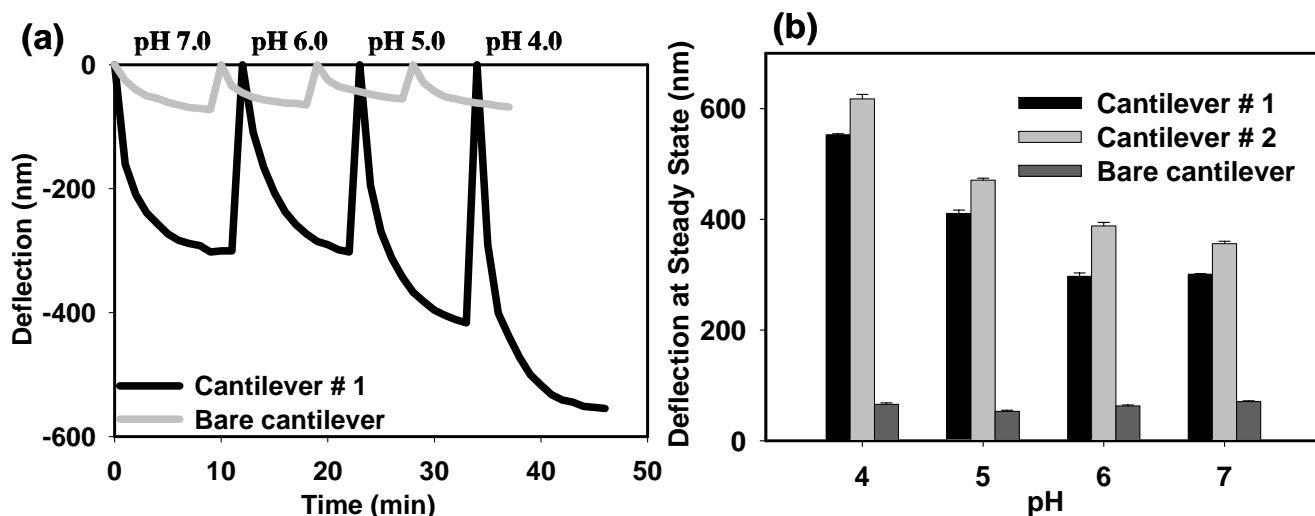
Figure 4. (a) A comparison between the bending of a micro-cantilever decorated with pH sensitive pNIPAAM-VI brush (black line) grown for 15 minutes and a bare, gold coated cantilever (gray line) as a function of pH. (b) A histogram of the absolute steady state deflections of two micro-cantilevers decorated with pNIPAAM-VI polymer brushes measured as a function of pH in the range from 4 to 7. The deflection values of a bare cantilever are shown also in different pH for comparison purposes.

conditions, and that it is a relatively inexpensive technique. Polymer nanopatterning, as demonstrated here, could be of significant importance as switches in nano- and microfluidic devices.

We show that micro-cantilevers decorated with an SRP brush layer can be successfully used as pH and solvent type sensors. The use of SRP coated micro-cantilevers promise great potential for sensing and actuation applications in micro-fluidic and Bio-MEMS devices because of the unique way by which SRP amplify molecular binding events and changes in the liquid environment. Based on this research, we anticipate that micro-cantilevers decorated with the specific sequence of short peptide, will detect and transduce the binding of spores of some *Bacillus* species which comprise one branch of the *Bacillus* phylogenetic tree. Our results so far demonstrate that micro-cantilever deflection can be used effectively for the sensitive detection of molecular recognition events, encouraging use of this technique as a rapid response biosensor.

ACKNOWLEDGMENTS

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